

SEDIMENT DYNAMICS IN THE CASTLETON KARST, DERBYSHIRE, U.K.

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ABSTRACT

Chemical and mineralogical data are presented for a suite of 59 sediment samples collected from the P8 and Speedwell cave systems (and mineralogical data are presented for a further six surface sediments) in the Castleton karst catchment, Derbyshire, England. Sediments are grouped according to age and depositional environment and these groups show distinctive mineralogical and chemical characteristics. Clay mineralogy is effective at distinguishing different sediment sources for ancient and modern sediments which are derived from pre-Devensian tills and Devensian solifluction deposits, respectively. Major element chemistry reflects these differences in clay mineral content, while trace elements demonstrate the importance of abrasion of ore minerals in conduits in the aquifer which follow mineral veins, even under natural, pre-mining conditions. Clay minerals are confirmed as the host for uranium in uranium-rich ancient sediments. Consideration of organic carbon and hydrogen concentrations shows that plant material is the dominant source of organic material in the modern sediments. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS: sediment dynamics; clay mineralogy; turbulent flow; sediment sources

INTRODUCTION

Because a substantial proportion of groundwater movement in mature karstic systems is achieved by turbulent flow in solutionally enlarged conduits, it is possible for sediment to be redistributed through the aquifer, especially during flood events when flow velocities may significantly exceed 1 m s^{-1} . The dynamics of sediment in karst groundwater systems is, however, a topic which has received relatively little attention. The mineralogy and chemical composition of sediments can potentially yield information on sediment provenance and transport processes occurring within the sediment after its accumulation, and the presence of soluble or reactive components which might be leached from the sediment into porewater or groundwater. We report here the results of a study of the mineralogy and geochemistry of a suite of sediments from the Castleton karst system, Derbyshire, England; we use these data to constrain sources of sediment in different parts of the system and discuss how their relative importance has changed. We also examine some of the changes occurring in the sediment as a result of post-depositional microbial activity.

Geology and hydrology of the Castleton karst catchment

The geology and hydrology of the Castleton karst catchment are portrayed in Figures 1 and 2. The karstic aquifer is formed in limestones of Dinantian age and though several sedimentary facies are present they can be considered as a single hydrogeological unit. The limestone is overlain on the west side of the catchment by the Namurian age Edale Shales, a sequence of mudstones, siltstones and sandstones. The boundary is not well exposed, lying along the valley of Rushup Vale, which is infilled with Quaternary solifluction deposits (Johnson, 1967). Soils on the limestones of the catchment are predominantly derived from loessic materials

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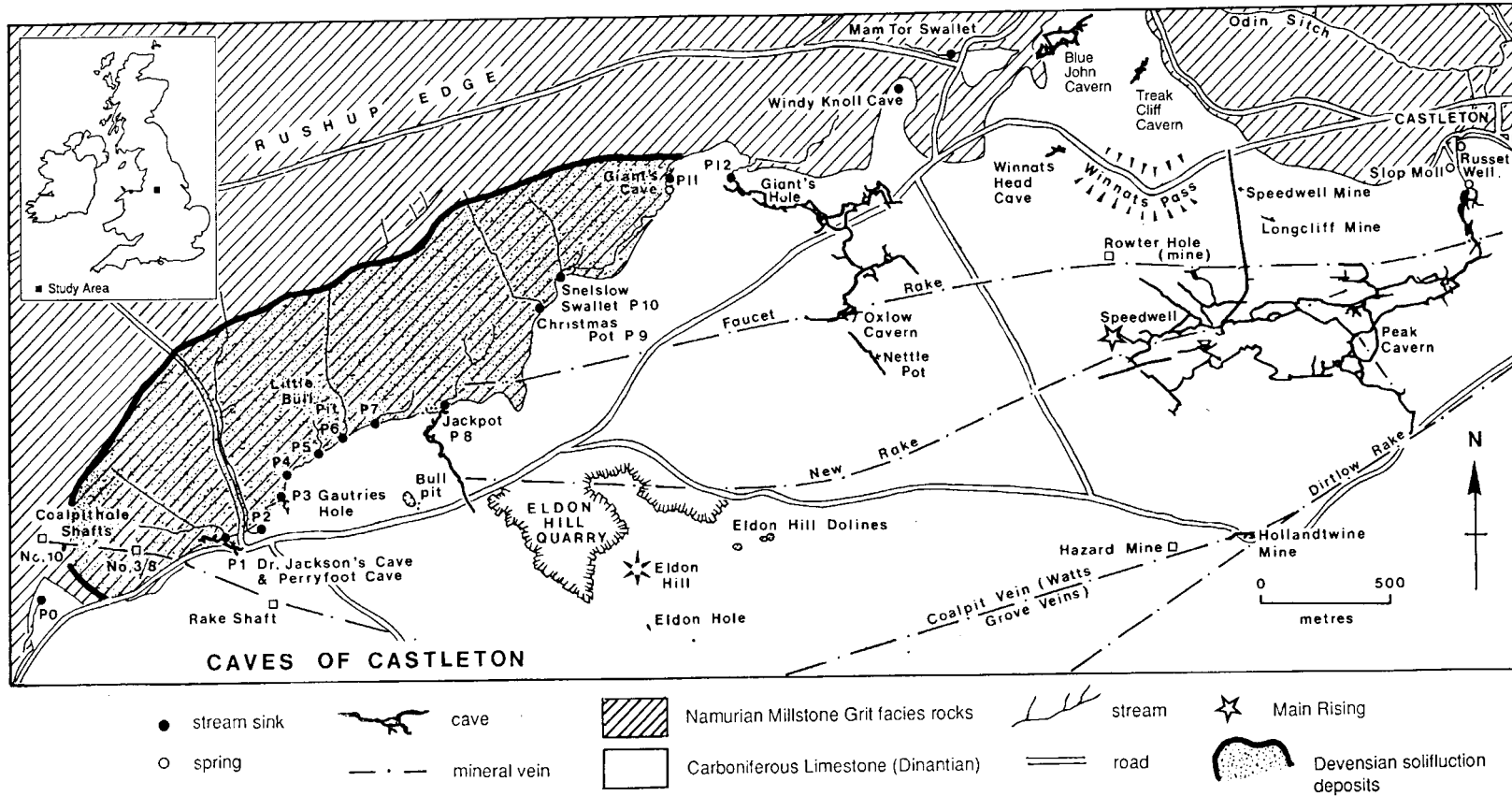


Figure 1. Geology, hydrology and caves of the Castleton catchment

SCHEMATIC HYDROLOGICAL SYSTEMS DIAGRAM FOR THE CASTLETON KARST

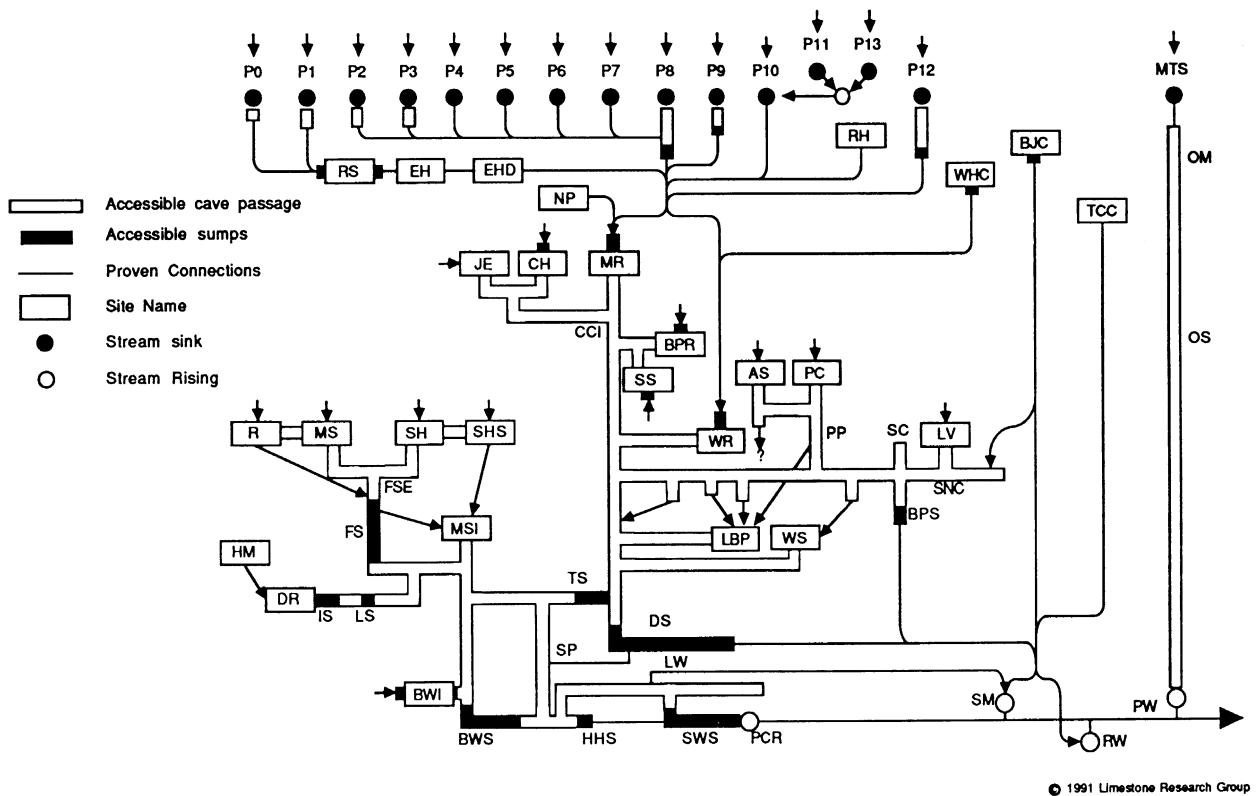


Figure 2. Summary of drainage routes within the Castleton karst, based on water tracing experiments (Gunn, 1991). Key: AS, Assault Course; BPS, Bottomless Pit Sump; BRP, Bathing Pool Rising; BJC, Blue John Cavern; BWI, Buxton Water Inlet; BWS, Buxton Water Sump; CCI, Cliff Cavern Inlet; CH, Cliff Hanger; DR, Dooks Retreat; DS, Downstream Sump; EH, Eldon Hole; FS, Far Sump; FSE, FS Extension; HHS, Halfway House Sump; HM, Hollandtwine Mine; IS, Ink Sump; JE, Joint Evert; LBP, Long By-Pass; LV, Longcliffe Vein; LW, Lumbago Walk; MR, Main Rising; MS, Minor Sump; MSI, Main Stream Inlet; MTS, Mam Tor Swallet; NP, Nettle Pot; OM, Odin Mine; OS, Odin Sough; PO to P13, Rushup Edge Swallets; PCR, Peak Cavern Resurgence; PP, Pilkington's Passage; PW, Peakshole Water; R, Rasp Stream; RH, Rowter Hole; RS, Rake Shaft; RW, Russett Well; SC, Speedwell Cavern; SH, Stemple Highway; SHS, SH Sink; SNC, Speedwell Near Canal; SM, Slop Moll; SP, Speedwell Pot; SS, Secret Sump; SWS, Swine Hole Sump; TCC, Treak Cliff Cavern; TS, Treasury Sump; WHC, Winnats Head Cavern; WR, Whirlpool Rising; WS, Window Sump

(Piggot, 1962). In other parts of the area, remnants of tills from older, pre-Devensian glaciations are present (e.g. Burek, 1991).

Water from catchments on the shale sequence cut valleys in the Quaternary deposits before entering the aquifer along its northwestern flank at 12 distinct points. Nine of these sinking streams are associated with influent caves (e.g. P8 (or Jackpot) cave sampled in this study) which drain to sumps. Results of water tracing experiments (Ford, 1966; Gunn, 1991) are summarized in Figure 2. All the allogenic water drains to Speedwell Cavern, probably via phreatic conduits developed along subvertical mineralized faults ('rakes') which trend E–W and SW–NE across the limestone. The mineralization in these veins consists primarily of a calcite and barite (BaSO_4) gangue with galena (PbS) and sphalerite (ZnS) ore minerals which in places have been mined (Worley and Ford, 1977). The water rising in Speedwell Cavern flows for about 1000 m being augmented en route by autogenic percolation water from Cliff Cavern and other minor tributaries. At the downstream limit the water enters another flooded conduit at Downstream Sump, eventually emerging at the surface from Russett Well and Slop Moll, which are interconnected risings on opposite banks of Peakshole Water (Figure 2). Much of the accessible passage in the Speedwell/Peak Cavern system is abandoned and drained phreatic conduit, in places infilled with clay-rich sediments which form part of this study. These

passages fed a vauculian spring at Peak Cavern before downcutting in the Hope valley lowered local base levels and initiated incision of vadose passage below the abandoned phreatic system (Ford, 1977; Waltham *et al.* 1997).

Sediments of the Castleton karst

Within the catchment of the Castleton karst aquifer there are a variety of potential sediment sources.

- (1) *Allogenic sources.* Sediment may enter the aquifer with the allogenic waters which recharge the aquifer in the Perryfoot region. These may therefore be derived either by erosion of the Edale Shale bedrock sequence or from the Quaternary deposits into which the sinking streams have incised valleys leading to the swallet caves.
- (2) *Autogenic sources.* Potential sources of sediment in the limestone aquifer itself comprise the following.
 - (2a) *Limestone.* As the accessible cave passages and other solutionally enlarged conduits within the limestone aquifer develop, limestone may be supplied to the sediment. This is evident within the accessible caves as boulders resulting from roof collapse. Attrition of these boulders and the passage walls by moving sediment can supply finer-grained limestone to the sediment reservoir. Dissolution of the limestone may also contribute a residue of insoluble material, usually clays, to the sediment budget.
 - (2b) *Mineral vein components.* Since the major conduits and parts of the accessible cave passage follow mineralized faults or 'rakes' within the limestone, there are additional insoluble mineral phases which might be eroded and contribute to the sediment load, especially the minerals barite, galena and sphalerite. Within the Speedwell system, mining activity may also have generated sediment containing these mineral components.
 - (2c) *Soils on the limestone.* The whole of the autogenic catchment is covered by soils, largely derived from loessic parent materials. Soil materials may be transmitted to cave systems by autogenic percolation waters (Hardwick and Gunn, 1990).

Within the aquifer, sediments can only be sampled from the accessible cave passages. The active stream passages in the influent caves generally have very coarse-grained sediments (gravel, cobble and boulder sizes) and similar sediments are distributed along the active streamway of Speedwell Cavern. The only significant quantities of finer-grained sediment associated with the active streamway in P8 were located in the first downstream sump pool (though there are banks of ancient fine-grained sediment in passages which no longer receive active stream flow). However, within Speedwell Cavern the main stream passage is sufficiently wide and tortuous to contain sheltered areas where finer-grained sediments (mostly sand and silt) can accumulate. In particular the Far Canal, which was excavated by miners in the late 18th century, provides a relatively sheltered environment where significant quantities of silt and fine sand have accumulated in banks. Speedwell Cavern also has high-level passages which no longer receive active stream flow and contain banks of ancient fine-grained sediments. Ancient sediments are defined for the purposes of this work as those which were deposited in the past and are not in equilibrium with the present hydrology due to lowering of the base level in the aquifer.

SAMPLING SITES

Loessic-derived soil samples were taken from a pit dug into the soil profile on the limestone above the entrance to P8 cave. Samples of the solifluction materials in Rushup Vale were collected from the sides of three of the valleys incised into them by influent streams. Cave sediments were collected in P8 cave and in Speedwell Cavern. Details of all the samples and sites are given in Table I and Figure 1. In P8 the sediment accumulation in the first downstream sump was exposed by lowered water levels following a period of dry weather in the summer of 1989. An inspection pit was dug which exposed a 40 cm deep section; whilst much of the bank consisted of cobbles and gravel, samples were taken from horizons consisting of finer-grained material (Table I). A series of core samples was taken in sediment banks (Speedwell Cavern sites 1–7; Table I, Figure 1) by pressing plastic tubes, 15 cm long and 7 cm in diameter, into the sediment at right angles to the

Table I. Details of samples collected

Sample ID	Sediment Group	Location/Comments
LO-1	Loess	30 cm
LO-2	Loess	60 cm
LO-3	Loess	80 cm
P4g	Solifluct.	} Samples collected from solifluction deposits in the catchments of three insurgent streams.
P5g	Solifluct.	
P6g	Solifluct.	
SPW-1	I	Core taken in main stream passage, SC. A,B and C are 0–4, 4–8 and 8–12 cm depth intervals.
SPW-2	III	Core in sediment bank in Bathing Pool Passage, SC. A,B and C are 0–4, 4–8 and 8–12 cm depth intervals.
SPW-3	II	Core in sediment bank in Far Canal, SC. A,B and C are 0–4, 4–8 and 8–12 cm depth intervals.
SPW-4	II	Core in sediment bank in Far Canal, SC. A,B and C are 0–4, 4–8 and 8–12 cm depth intervals.
SPW-5	II	Core in sediment bank in Far Canal, SC. A,B and C are 0–4, 4–8 and 8–12 cm depth intervals.
SPW-6	II	Core in sediment bank in Far Canal, SC. T,A,B and C are 0–1, 1–4, 4–8 and 8–12 cm depth intervals.
SPW-7	II	Core in sediment bank in Far Canal, SC. T,A,B and C are 0–1, 1–4, 4–8 and 8–12 cm depth intervals.
SPW-8	I	Sediment scraped from boulders, main stream passage, SC.
SPW-9	-	Wood fragment from 14 cm depth in sediment in Far Canal, SC.
CC-1 to CC10	III	Samples collected at 3 cm intervals from fine-grained sediment bank in Cliff Cavern, SC.
P8-1A	P8	5.5 cm
P8-1B	P8	5.5 cm
P8-2A	P8	11 cm
P8-2B	P8	11 cm
P8-3A	P8	17 cm
P8-3B	P8	17 cm
P8-X	P8	10 cm
P8-XI	P8	30 cm
P8-XVI	P8	14 cm

SC = Speedwell Cavern.

sediment surface. The tube and the enclosed, relatively undisturbed sediment were withdrawn and capped for transport. In the laboratory the cores were extruded and sliced lengthwise for inspection. All showed crude subhorizontal lamination on a scale of a few millimetres and some were bioturbated in the top 1–2 cm. At site SPW-8 a thin veneer of sediment was found on boulders in the main streamway but above the normal water level. This must have been deposited during a recent flood event and was collected by scraping into a wide-mouthed plastic container. In Cliff Cavern, Speedwell, a series (CC-series) of samples was taken from a vertical face of a sediment bank by pressing a series of smaller plastic tubes horizontally into the face. Ten samples were collected at approximately 3 cm intervals, the total height of the section sampled being 30 cm. The samples collected in Speedwell Cavern thus came from a variety of sedimentary environments and are subdivided into three groups:

- (i) Group I samples are from the main streamway in the upstream part of the cave (and importantly upstream of the boulder piles below James Hall's Engine Mine, the furthest upstream mineral workings in the Speedwell system) and comprise core SPW-1 and sample SPW-8;
- (ii) Group II samples are from cores SPW-3 to SPW-7 from the flood overflow passage of Far Canal, downstream of the mineral workings in the mine and therefore potentially contaminated with ore and gangue minerals from within the Cavern;
- (iii) Group III samples are from core SPW-2 and the CC-series samples from banks of ancient sediment in high-level passages. The age of these sediments is not well constrained, but they significantly pre-date

mining activities in the area since abandonment of these passages was a natural phenomenon and not caused by mine dewatering. Comparison with surficial deposits may shed some light on their age. Sample SPW-9 was not a sediment but a wood fragment 80 mm in length recovered from a depth of *c.* 14 cm in sediment in Far Canal. It had a distinct blackened crust which covered the surface to a depth of *c.* 1 mm. The fragment was dried (105°C) and a small amount (*c.* 2 mg) of the crust scraped off for elemental analysis of sulphur.

SAMPLE PREPARATION AND ANALYTICAL DETAILS

Core samples were subsampled at the depth intervals indicated in Table I. All samples were air dried at 90°C. Samples from P8 which contained coarse material were sieved through a 1.6 mm sieve and all analysis was carried out on the fines fraction. All samples and subsamples were then disaggregated and homogenized and a small aliquot separated for X-ray diffraction (XRD) analysis. The remainder was crushed to pass 120 mesh and homogenized.

X-ray diffraction analysis

The uncrushed sediment was crushed briefly under water in an agate mortar and pestle and a small amount of the resulting suspension was pipetted onto a glass slide and left to evaporate at room temperature. Diffractograms of the sediment on the slides were obtained using an automated PW1840 diffractometer with a PW1830 generator producing Cu-K α radiation.

X-ray fluorescence analysis

Dried crushed sediment (0.40 g) was accurately weighed and ignited at 1000°C for 1 h and reweighed to determine loss on ignition (LoI) before fused beads were prepared for major element analysis using an adaption of the method of Norrish and Hutton 1969. Trace elements were analysed on pressed pellets made from the crushed sediment and a PVA binder. Analyses were made on a Phillips PW1400 X-ray spectrometer with a Rh tube, calibrated against international reference materials. Errors are 1 percent relative or better for major elements and 5 percent relative or better for traces.

C, H, S elemental analysis

Elemental analyses were made on a Carlo Erba 1106 analyser. S was determined directly on the crushed sediment. Subsamples for organic carbon (C_{org}) and total H analysis were weighed and treated with *c.* 1M HCl for 2 h (to remove inorganic carbon present as calcite), rinsed, dried, reweighed and rehomogenized prior to analysis. Weight loss on HCl treatment was calculated (this corresponds approximately to calcite content) and was used to correct C_{org} and H analyses to the original sample weights.

RESULTS

Sediment description

The physical characteristics of the samples analysed are summarized for each group in Table II. Polymineralic clasts in the larger grain size fractions (present only in the P8 samples and Core 1 from Speedwell main streamway) were dominantly of yellow and brown sandstone with lesser quantities of grey and dark grey mudstone/shale and siltstone. The proportion of mudstone/shale and siltstone clasts was higher in the P8 sediments than in Core 1 (cf. Murphy, 1993).

The fine-grained Group III sediments exhibit well-developed millimetre-scale lamination, suggesting that they have not been affected by bioturbation.

Table II. Physical characteristics of cave sediment samples

Sample type	P8 sump	Group I	Group II	Group III
No. of analyses	9	4	16	13
Description	Sand-gravel	Silt-fine sand	Silt-fine sand	Clay-silt
Wt% in range:				
<0.1 mm	0–1	8–22	11–20	97–100
0.1–0.5 mm	19–48	60–78	50–80	0–3
0.5–1.6 mm	36–51	0–30	0–29	0
>1.6 mm*	0–45	0	0	0

* Coarse fraction rejected for mineralogical and chemical analysis

Mineralogy

Minerals were identified from diffractogram peaks using data from the *Powder Diffraction File* search manuals (JCPDS, 1980). First the main peaks of the minerals calcite, quartz, illite, smectite and kaolinite were sought to identify the presence of these common minerals. If any mineral was present, all minor peaks which might be associated with that mineral were excluded from further consideration. Further mineral identifications were made from any significant residual peaks. Clay mineral assignments were checked on representative portions of samples using standard glycolation and heat-treatment techniques. Minerals identified in those samples analysed are listed in Table III.

The loessic soil samples are dominated by quartz, with significant chlorite in all three and minor illite in LO-2 only. The solifluction deposits are also dominated by quartz but contain illite and kaolinite with no chlorite. All of the cave sediments analysed contain quartz; calcite is found in many of the modern sediments from the active stream sites (P8 and Groups I and II from Speedwell) but is detected in only one of the fine-grained ancient sediment samples (SPW-2A). Calcite is probably derived by attrition of passage walls and limestone blocks. The different groups of samples have distinctive clay mineralogies, and the relative size of characteristic XRD peaks has been used to classify the relative proportions of these minerals. Peak size is a function of grain size and sample preparation as well as the amount of mineral present, so such an assessment is crude and is restricted here to the classes 'absent', 'minor' (weak peaks), 'present' and 'dominant'. Smectite is rare in all modern sediment samples but more common in the ancient sediments and kaolinite is present in the P8 samples and ancient sediments but not in the modern sediments from Speedwell. The CC-series samples exhibit variable clay mineralogy through the profile sampled. At the top of the sequence (samples 1 and 2) they contain all three clay minerals and are very similar to the SPW-2 core samples from Bathing Pool passage. Lower down (samples 3, 4 and 5) all clay mineral peaks are smaller and illite and kaolinite are not detected in some samples, whilst at the base of the profile (samples 6–10) illite and smectite are again present but kaolinite is more dominant than at the top of the profile.

The only other mineral positively identified was barite in sample SPW-7C (where there are high concentrations of Ba as well as Pb and Zn; see below). However, detection limits for minerals by XRD vary from 2 to 10 per cent (depending on mineral, grain size and preparation) and other peaks were often present but impossible to identify uniquely. Small proportions of other minerals are certainly present, but the dominant mineralogy has been characterized.

Chemistry

For reasons of space, the full analytical data set is not presented but summary data are given in figures and tables. The major elements (including Ba as BaO is a significant component of some samples) and LoI are combined to give the analytical total, which gives an indication of the accuracy of the analysis. The trace elements not present at high enough concentration to affect the total and C_{org} and S are not included as these components are generally considered volatile on ignition and make up part of LoI (along with water lost by dehydration reactions and CO₂ lost by calcining of calcite). Many samples have totals within the quoted error of 1 per cent on 100 per cent, but others are as low as 93–97 per cent and these have high Ba and heavy metal concentrations. These low totals probably do not reflect analytical inaccuracy but rather the assumption that S

Table III. Mineralogical composition of sediments determined by X-ray diffraction

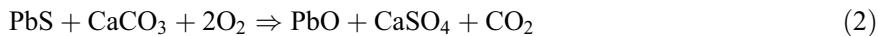
	Quartz	Calcite	Smectite	Illite	Kaolinite	Other minerals
Loessic soil						
LO-1	XX	—	—	—	—	Chlorite
LO-2	XX	—	—	x	—	Chlorite
LO-3	XX	—	—	—	—	Chlorite
Solifluction deposit						
P4g	XX	—	—	X	x	—
P5g	XX	—	—	X	x	—
P6g	XX	—	—	X	x	—
Group I						
SPW-8	X	X	—	X	x	—
Group II						
SPW-6A	X	X	x	X	—	—
SPW-7A	X	—	—	X	—	—
SPW-7B	X	X	—	X	—	—
SPW-7C	X	X	x	X	—	Barite
Group III						
SPW-2A	X	X	X	X	X	—
SPW-2B	X	—	X	X	X	—
SPW-2C	X	—	X	X	X	—
CC-1	X	—	X	X	X	—
CC-2	X	—	X	X	X	—
CC-3	X	—	X	X	—	—
CC-4	X	—	x	—	x	—
CC-5	X	—	x	—	X	—
CC-6	X	—	X	X	XX	—
CC-7	X	—	x	X	XX	—
CC-8	X	—	X	X	XX	—
CC-9	X	—	X	X	XX	—
CC-10	X	—	X	X	XX	—
P8 sump						
1A	X	X	x	—	XX	—
2A	X	—	x	XX	X	—
3A	X	—	—	X	X	—
X	X	—	—	X	X	—
XI	X	X	—	X	X	—
XVI	X	X	x	X	X	—

Key: —, absent; x, weak peaks; X, present; XX, dominant

is lost on ignition and is not included in the total. Ba is probably present as barite (BaSO_4) which is resistant to heating to 1000°C , yet Ba is accounted for as BaO in the totals, and a deficit will arise from the unaccounted SO_3 . Ignition is also assumed to produce metal oxides and SO_2 from sulphide minerals, e.g.



However, when calcite is present (as it is in most samples analysed) SO_2 may be fixed as anhydrite and not lost from the sample:



thus similarly leading to low analytical totals for major element species and LoI.

Table IV. Means and standard deviations (s.d.) of major element data for different sediment groups

	Group I		Group II		Group III		P8	
	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.
SiO ₂	79.90	7.01	69.27	9.51	63.99	4.18	77.69	1.41
TiO ₂	0.38	0.06	0.48	0.07	0.99	0.08	0.38	0.04
Al ₂ O ₃	5.91	0.68	8.30	1.24	16.79	2.61	8.43	0.43
Fe ₂ O ₃	3.46	0.47	4.53	0.75	5.99	0.71	4.99	0.74
MnO	0.11	0.01	0.21	0.06	0.13	0.04	0.15	0.04
MgO	0.26	0.06	0.43	0.09	1.11	0.16	0.41	0.02
CaO	2.40	2.56	4.19	3.11	0.72	0.04	1.09	0.32
Na ₂ O	0.67	0.17	0.76	0.12	0.86	0.18	0.49	0.13
K ₂ O	0.75	0.07	1.03	0.15	2.36	0.25	1.05	0.05
P ₂ O ₅	0.18	0.04	0.25	0.06	0.21	0.04	0.23	0.03

DISCUSSION

Mineralogy

The loessic soil samples have a distinctive mineralogy compared to all other samples, in that they contain chlorite as their primary clay mineral. None of the cave sediments (modern or ancient) contains detectable chlorite suggesting that erosion of the soils on the limestone and transport into the aquifer with autogenic recharge is not, nor has been, a major source of sediment to the caves, confirming the findings of Hardwick and Gunn (1991). The illite- and kaolinite-dominated clay mineral compositions that dominate the modern cave sediments (P8 and Groups I and II in Speedwell) correspond well with the solifluction deposits. They are therefore most likely derived by their erosion, though weathering of the mudstones on Rushup Edge in the headwaters of the sinking streams could produce similar material. The Group III ancient sediments contain a far greater proportion of smectite than any of the other samples which may indicate that their genesis was related to surface conditions significantly different to those of the present day. Burek 1991 gives mineralogical compositions for two types of pre-Devensian tills in this area: her 'older till' contains significant smectite whereas her 'younger till' does not; both contain kaolinite. The most probable source for the ancient sediments would thus be erosion of the previously more extensive 'older tills' which were probably of Anglian (or older) age. Such an origin fits well with abandonment of the old phreatic passages in the Ipswichian as proposed by Waltham *et al.* 1997. Sediment derived from Anglian till transported into the aquifer via the old phreatic passage system early in the Ipswichian (or possibly during an earlier interglacial) would then be preserved as the phreatic passages were abandoned.

Major element compositions

Means and standard deviations for the major element species in each of the sediment groups are given in Table IV and statistically significant differences between groups indicated in Table V. The data exhibit either strongly significant differences (significant at the 90 per cent confidence limit or higher) or else there was no significant difference; there were thus no 'marginal' cases. The Group III sediments are the most chemically distinctive, showing large enrichments in Al₂O₃, Fe₂O₃, MgO and K₂O. Whilst there are some significant differences in concentrations of these species between other groups, they are never so large. Group III sediments are also enriched in TiO₂ compared to the other groups which otherwise show no significant differences between them. SiO₂ shows a large and significant depletion in Group III compared to the others. Al, Fe, Mg and K are all components of clay minerals and these differences reflect the relative dominance of clay minerals in these sediments. The relative depletion in SiO₂ reflects the lessened significance of detrital quartz in these finer-grained, clay-rich sediments (see Table II and Mineralogy section). The Group II sediments are also significantly, but less markedly, enriched in Al, Fe, Mg and K and depleted in Si compared

Table V. Differences in means and confidence levels for statistically significant differences in major element data between sediment groups

	I–II		I–III		I–P8		II–III		II–P8		III–P8	
	m ₁ –m ₂	conf. level	m ₁ –m ₂	conf. level	m ₁ –m ₂	conf. level	m ₁ –m ₂	conf. level	m ₁ –m ₂	conf. level	m ₁ –m ₂	conf. level
SiO ₂	10.6	98.0	15.9	99.9					–8.4	99.0	–13.7	99.9
TiO ₂			–0.61	99.9			–0.51	99.9			0.61	99.9
Al ₂ O ₃	–2.39	99.5	–10.9	99.9	2.52	99.0	–8.49	99.9			8.36	99.9
Fe ₂ O ₃	–1.07	96.0	–2.53	97.0	–1.53	97.0	–1.46	97.0			1.00	90.0
MgO	–0.17	99.9	–0.85	99.9	–0.15	99.9	–0.58	99.9			0.70	99.9
CaO					1.31	90.0	3.47	99.9	3.10	99.9	0.37	99.0
K ₂ O	–0.28	99.8	–1.61	99.9	–0.30	99.0	–1.33	99.9			1.31	99.9

Blank entries indicate no statistically significant difference in means. No significant differences were found between any groups for MnO, Na₂O and P₂O₅. Significance is calculated using the variance associated with each sample population combined with the variance associated with the analytical error on each datapoint. Errors used for the latter were 1 per cent relative or 0.05 weight per cent, whichever was greater.

to Group I, again correlating with finer grain size (Table II) and probably due to preferential accumulation of clay-sized material in the more sheltered depositional environment offered by Far Canal. Group I sediments also exhibit some significant differences to P8 sediment, but these are yet smaller in magnitude and show no consistent pattern with respect to clay mineral components versus silica.

No groups showed significant differences for MnO, Na₂O or P₂O₅, which were all present at low concentrations. CaO concentrations showed wider scatter than other elements; this is related to detrital calcite content. Although some groups showed significant differences, there is little systematic change.

Ore mineral components

Since the groundwater conduits in the Castleton karst follow mineralized faults and many of the samples were collected in Speedwell Cavern, where there are further mineral veins present which have been actively mined, it is distinctly possible that mineral constituents of the vein fillings may be included in the sediments sampled. In addition to calcite, which is present throughout the system in the limestone wallrocks, the main mineral vein constituents are barite (BaSO₄), galena (PbS) and sphalerite (ZnS) (Worley and Ford, 1977). Figure 3 shows plots of the Zn, Pb and Ba concentrations of the sediments by group. In all cases the concentrations of these species are uniformly low in the P8 sediments, while the modern Speedwell sediments show higher concentrations with a general trend to increasing concentrations downstream, with Group II higher than Group I. This suggests that either sedimentary sorting is taking place, with these denser minerals becoming concentrated by physical processes in certain depositional environments, or else mineral vein material is being added to the sediment progressively both between sinks and resurgence in Speedwell and within Speedwell Cavern itself. To test for the possibility of sedimentary sorting, Zr concentrations are also plotted in Figure 3. Zr is associated with another heavy mineral, zircon, and should follow the same pattern if sedimentary sorting is the primary control on the distribution of these species. In fact the pattern of Zr concentrations is by no means so clear cut, with overlap between the three groups of samples, so addition of vein mineral components is highly probable. Within Speedwell Cavern the most probable cause is mining operations during the period of active exploitation of the veins. Anthropogenic processes could also apply to material added during the transit from sinks at Perryfoot to rising in Speedwell, because there were workings on the Coalpithole rake at Perryfoot. However, the Group III ancient sediments pre-date any mining activity and have concentrations that range to values much higher than the present P8 inputs (especially for Pb and Zn; Figure 3). Their Zr concentrations do not differ from the range of the other sediment types, again implying that sedimentary sorting is not the primary process controlling the concentration of these minerals. This provides important evidence for the input of significant amounts of material from the mineral veins to the sediment budget of the system under natural, pre-mining conditions. Sulphur is the other major constituent of

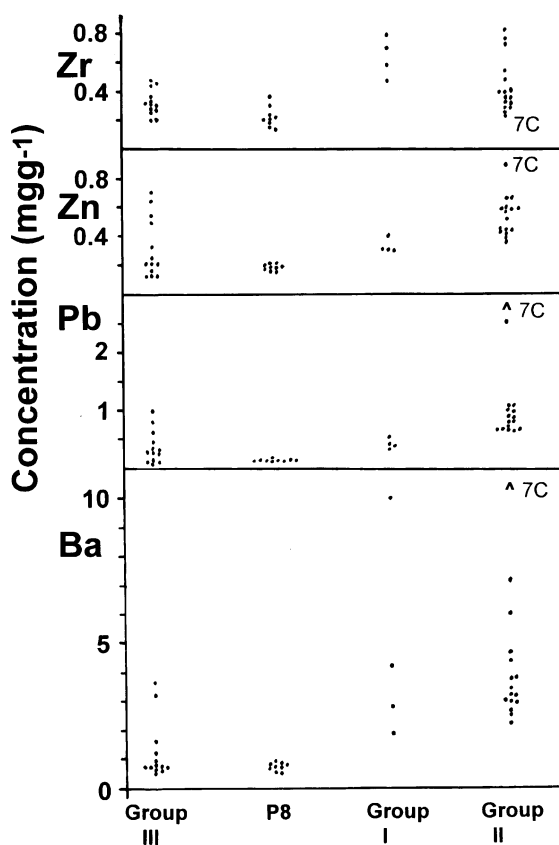


Figure 3. Variation of concentration of Zr and of the ore-mineral components Zn, Pb and Ba in sediments of different groups. Sample 7C is identified and is off-scale for Ba (76 mg g^{-1}) and Pb (13.7 mg g^{-1})

these ore-derived minerals, but is not determined nearly so precisely as the metals. In general, S correlates with Ba (the most abundant of the ore-derived elements; $r = 0.73$, but significant at the 99 per cent confidence level) tending to confirm that Ba is present as BaSO_4 . The error/detection limit of S analysis is such that it is impossible to be certain whether Pb and Zn are now present as sulphides or a chemical weathering product of the original ore sulphide.

Sediment sources to the ancient deposits

The presence of smectite in the ancient sediments was used to constrain their source to pre-Devensian tills. However, the sequence in Cliff Cavern exhibits significant changes of mineralogy (Table III, CC-1 to CC-10) and trace element chemistry (Figure 4) with depth. The topmost part of the sequence (CC-1 and CC-2) is similar to the sediment sampled in Bathing Pool passage (core SPW-2) with significant illite, smectite and kaolinite present. Below this (CC-3 to CC-5) there is a marked increase in the concentrations of Pb, Zn, Ba and a less pronounced increase in Zr. This association suggests an enrichment in heavy minerals at this level and correlates with an absence of illite and decreased peak sizes of smectite and kaolinite. Silica concentration is highest and Al concentration lowest in sample CC-4 from this level, indicating a relative depletion in clays and enrichment in quartz at this horizon. Below this level (CC-6 to CC-10) heavy metal concentrations are lower than at the top of the core and kaolinite is the dominant clay mineral by XRD. These data indicate changing conditions of sediment supply and accumulation. A possible interpretation is that the high heavy metal/heavy mineral concentrations represent a period of sediment starvation and winnowing,

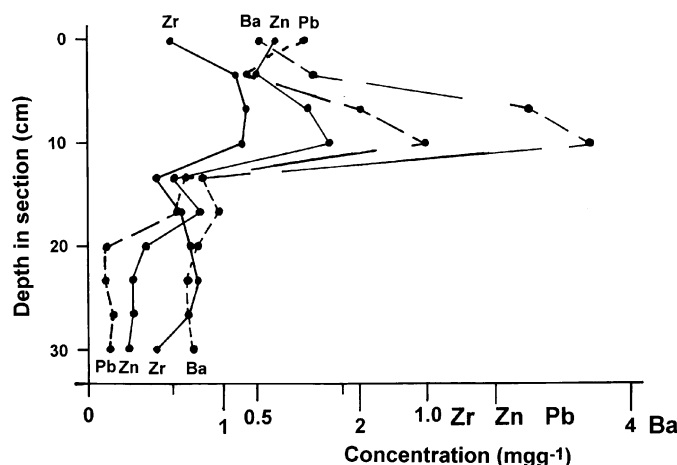


Figure 4. Variation of concentration of Zr and of the ore mineral components Zn, Pb and Ba in the Cliff Cavern sediment bank profile

removing clays but not heavy minerals, between two periods of sediment supply from different sources, as distinguished by their different clay mineralogies.

Uranium

The Group III ancient sediments are significantly enriched in U relative to all others (mean 18.3, standard deviation 3.1 ppm vs. 2.7 ± 0.9 ppm, significantly different at the 99.99 per cent confidence level) and are a significant potential source of radon in the cave environment (Bottrell, 1991). Bottrell (1991, 1993) addressed the question of the mineralogical host for U in these sediments and concluded that the correlation between U and K, Al and Mg indicated a clay mineral host. The fuller data set here enables comparison with elements which might be characteristic of other U hosts. Neither Zr nor P correlate with U, so zircons or phosphate minerals are unlikely to host U, but a correlation between Ti and U ($r = 0.95$, significant at the 99.9 per cent confidence level) might indicate rutile or sphene as an alternative host to clays. However, the Ti itself could be resident in one or more clay minerals; illite in particular can contain substantial Ti (Deer *et al.* 1966).

Organic carbon

Organic carbon (C_{org}) was detected in all of the sediments at variable concentrations. The Group III ancient sediments contained 0.35 to 0.77 weight per cent, while samples from P8 sump contained 0.34 to 1.07 weight per cent. The recent sediments from Speedwell contained 0.01 to 3.37 weight per cent and the concentration decreases markedly with depth in many of the cores taken in Far Canal. The sources of C_{org} and its depth profiles of concentration are dealt with fully by Bottrell (1996) who concluded that the carbon was derived from C_3 plants and that decreases in concentration with depth were the result of normal microbial mineralization processes, analogous to those in soils. Mineralization reactions of organic material were also found to be the major cause of variation in sediment hydrogen concentration, though there is also a component of hydrogen in mineral hydroxyl groups. The organic carbon and/or bacteria responsible for its breakdown form the basis of a food chain supporting inwashed populations of Oligochaetes (Thomas and Bottrell, 1992). Of note is the occurrence of high sulphur concentration (0.8 weight per cent S) on a blackened coating to a wood fragment recovered from the sediment in Far Canal (SPW-9). This coating probably results from the action of sulphide in the sediment pore-water on the wood, implying that, in addition to the oxic degradation processes envisaged by Bottrell (1996), sulphate reduction may also be occurring deeper in the sediments, producing sulphide. This observation may explain the fate of a stainless-steel spade which was left

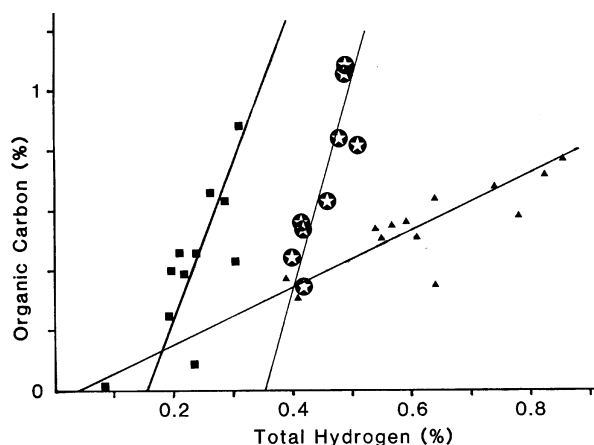


Figure 5. Plot of organic C vs. total H for different sediment groups. Key: squares, Speedwell Cavern modern sediments (Groups I and II); stars, P8 sump sediments; triangles, Group III ancient sediments

Table VI. Correlations between H and C_{org} for different sediment groups

Group	H/C (atomic ratio)	r	Significance (confidence limit, %)
P8	1.7	0.87	99
Speedwell*	2.4	0.77	98
Ancient seds (Group III)	12	0.83	99

* Those from Groups I and II with <1 weight per cent C_{org} which show no correlation between C_{org} and depth

standing in the sediment banks of Far Canal and which rapidly 'rotted away' (T.D. Ford, pers. comm.). Sulphidic pore-waters are aggressive to even the highest quality marine stainless steels and probably corroded through the spade.

The C_{org} data for the other samples are plotted vs. total H in Figure 5. The data fall into groups related to sediment type, each group forming a cluster with a good correlation between these parameters (Table VI). The P8 and Speedwell samples have slopes on the C/H plot which correspond to atomic H/C ratios close to 2. This is the value for modern plant material (cellulose, lignin, etc.) and these correlations confirm the conclusion of Bottrell (1996) that inwashed plant material is the major source of organic carbon in the Speedwell system. The intercepts of 0.16 and 0.35 weight per cent H correspond to hydrogen in mineral hydroxyl groups and are similar to the estimates of Bottrell (1996) of 0.2–0.3 weight per cent mineral H for some of the Far Canal sediments by different methods. The data for the Group III ancient sediments are markedly different. Although significantly correlated, these data have a slope (corresponding to atomic H/C = 12) which cannot represent an organic compound. Also the intercept (mineral H content) of the correlation line is far too small given that these are clay-rich sediments. This paradox is only resolved if the clay and organic contents of these sediments are themselves correlated, organic matter in these sediments being intimately associated with the clay mineral surfaces. In fluvial systems, organic carbon is commonly transported associated with mineral surfaces (Keil *et al.* 1994; Mayer, 1994) and the large surface area associated with clays makes clay surfaces the dominant agent of organic matter transport in fine-grained sediments. Indeed, Mayer (1994) found a consistent relationship between mineral surface area and associated

organic carbon of 0.86 mgC m^{-2} ; clay minerals characteristically have specific surface area $C. 15 \text{ m}^2 \text{ g}^{-1}$, giving surface-associated C_{org} concentrations of $C. 1.3$ per cent. This is similar to the C_{org} concentration of the Group III sediments, confirming the likelihood of association between clay mineral surfaces and organic matter.

CONCLUSIONS

The different sediment types sampled exhibit distinctive mineralogical and chemical characteristics. Modern stream sediments in the caves show similar mineralogy to the solifluction deposits in Rushup Vale and no relation to the distinctive loessic soils on the limestone. Sediment inwash with autogenic recharge does not therefore contribute significantly to the cave sediment budget. The Group III ancient sediments are richest in clay minerals and are the only group containing significant smectite, reflecting different sediment sources in the past, probably from Anglian tills. The clay mineralogy of the ancient sediment profile in Cliff Cavern exhibits a marked change, separated by a horizon with a concentration of quartz and heavy minerals. This, too, probably represents changing sediment supply and a period of sediment starvation and winnowing. The Group III sediments are also enriched in uranium, which appears to be associated with a clay mineral, rather than phosphate, zircon, rutile or sphene.

All the sediments contain some components (Ba, Pb, Zn) derived from the ore mineral veins which the phreatic parts of the system are thought to follow. In the modern sediments concentrations increase markedly downstream, a feature which almost certainly relates in large part to the mining activity in Speedwell Cavern. The increase in concentration of these components observed between P8 and Speedwell could also be due to mining activity on the Coalpithole rake. Importantly, the Group III ancient sediments which pre-date mining activity also show enhanced concentrations of these components, indicating that under natural conditions abrasion/weathering of the mineral veins associated with groundwater flow is a significant process.

Correlation between organic carbon and hydrogen concentrations in the modern sediments shows modern plant material to be the source of organic material, with an additional hydrogen source in the clay minerals. In the Group III ancient sediments the organic carbon must be associated with the clay mineral surfaces, as the correlation line gives very high H/C and would indicate a zero mineral hydrogen component. Transport of organic carbon on the surfaces of these fine-grained sediments can account for their organic carbon content.

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